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Effect of Catalyst $CeCl_3$ on $NaAlH_4$ for Hydrogen Desorption Kinetics

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Abstract:- Sodium alanate $NaAlH_4$ is complex hydride material for hydrogen absorption and desorption due to good storage capacity and good kinetic under temperature pressure conditions. The samples prepared doped catalyst $CeCl_3$ and $TiCl_3$with $NaAlH_4$ under argon atmosphere using ball milling and hand milling.Structural properties of sample are characterized by X-ray diffraction (XRD). Hydrogen capacity of sample is maximum 5.4 wt % which is obtained from the desorption kinetics at 250 ^oC using Seviert type apparatus. The rate of hydrogen desorption capacity increased with amount of catalyst.In this study, the Hydrogen desorption of $NaAlH_4$ doped with $CeCl_3$ and $TiCl_3$ is systematically studied.

Keyword:- *Sodium Alanate, Complex Hydrides, XRD, SEM and Seviert Type Apparatus for PCT.*

I. INTRODUCTION

Storage of energy in future are challenges due to shortage of fossils fuels and their CO_2 emissions. Hydrogen energy offers a solution to overcome both problems. In future,energy demands is covered by renewable energy sources like wind ,solar etc. hydrogen energy can be used as energy carrier with advantages like high energy density and emission free and conversion to electricity and using fuel cell and hydrogen energy can be store different type media such as solid , gas and liquid . Gas and liquid media are not suitable due to low volumetric and gravimetric density and lying space. Therefore solid media is suitable option for hydrogen storage. Hydrogen can be store in metal hydride, metal alloys and complex hydride etc. $NaAlH_4$ has become a promising candidate for the solid state storage of hydrogen due to discovery of the catalytic effect. nowdays researcher has been focused on the sodium alante due to doping of catalyst. The most effective dopant halides are particular $TiCl_3$ and $CeCl_3$ .Although most of complex hydrides show poor kinetics at relevant temperatures but the sodium alanate is one of the most suitable for hydrogen storage due to storage capacity and good kinetics for reversible hydrogen by adding a dopant under temperature and pressure conditions [1-3]. $TiCl_3$ is the most efficient catalyst due to a good cycle ability and high kinetics of doped $NaAlH_4$ which has been reported by Bogdanovic et al.[4-6].The decomposition of $NaAlH_4$ occurs through a multistep reaction according to the following equations and with a maximum hydrogen capacity 5.6 wt % with different catalyst.

$$3\,NaAlH_4 \leftrightarrow Na_3AlH_6 + 3\,Al + 3\,H_2 \quad (1)$$

$$Na_3AlH_6 \leftrightarrow 3\,NaH + Al + 3\,H_2 \quad (2)$$

$$2NaH \leftrightarrow 2\,Na + 2H_2 \quad (3)$$

First reaction occurs at 185 temperatures with 3.7 % and second reaction occurs at 250 temperatures with 1.9 % . The decomposition of NaH is not considered for applications because it occurs at high temperatures and pressure . Different group [7-9] have been reported that the decomposition as

$$3\,NaAlH_4 + TiCl_3 \rightarrow 3\,NaCl + 3\,Al^0 + Ti^{\,0} + 6\,H_2$$

The formation of NaCl through reaction shows the signature of vacancies. The role of the doping is to the investigation of the other compounds like $CeCl_3$, $TiCl_3$, $SeCl_3$. sodium alante desorbed hydrogen in two steps . Many researchers [10] have observed that the formation of Al_4Ce during cycling from the decomposition of $CeCl_3$ and sodium alanate $NaAlH_4$. Bogdanovic et al. [11] have shown that $CeCl_3$ remains mostly as a chloride compound after milling and cycling with $NaAlH_4$ and $CeCl_3$ is not decomposed during milling. Xiulin et.al.[12] is found that $CeCl_3$ is reused in the ball milling process and causing the formation of NaCl and Al-Ce alloy with a structure of $CeAl_4$. Borislav et. al. [13] show that $CeCl_3$ doped $NaAlH_4$ appears good candidate .Our motive is analyses to systematically performance of different dopant $TiCl_3$ and $CeCl_3$ for hydrogen desorption. the mixture of both dopant $TiCl_3$ and $CeCl_3$ is added to $NaAlH_4$ and improved kinetics of $NaAlH_4$.Structural characterization of sample is done by XRD . Kinetics of samples observed by PCT. The main objecte of this study is to investigate the effects of adding halides for hydrogen desorption of $NaAlH_4$ with catalyst.$CeCl_3$ and $TiCl_3$ were used is various amounts for the study.

II. EXPERIMENTAL METHOD

$NaAlH_4$ and catalysts $CeCl_3$ and $TiCl_3$ are used in this study and bought from Aldrich chemical Inc. The purities of materials are claimed 99%. Samples are prepared in an argon filled globe box due to sensitive to air and humidity. A planetary ball mill was used for milling of $CeCl_3$ and $TiCl_3$. The ball-milling was rotated speed of 350 rpm for 2 hour. $NaAlH_4$, $CeCl_3$ and $TiCl_3$ were weighed in glove box to avoid with oxygen and water content. The samples were covered by a kapton foil for structural characterization. Sample is characterized by XRD with Cu-K alpha radiation. The data were collected in the range between 30^o

and 80º with a step width of 0.02 at a rate of 2.5º /min. Hydrogen desorbed capacity is calculated in wt % .

III. RESULT AND DISCUSSION

Sodium alanate with 2 wt % catalyst $CeCl_3$ are analyzed by XRD using with Powder X and PCPDWIN program for structural characterization. sample is covered with a Kapton tape layer for safety from air and others factors. Fig (1) shows XRD pattern of dehydrogenated $NaAlH_4$ + 2% wt % $CeCl_3$.$NaAlH_4$ is appeared in Tetragonal structure which has lattice constant a=5.02, b=5.02 and c=11.34.$NaAlH_4$ is changed in Na_3AlH_6 at250ºC and Na_3AlH_6 is appeared in Monoclinic structure having lattice constant a=5.46, b=5.61, c= 7.80 and NaH in Cubic with lattice constant a=b=c=4.890 and $CeCl_3$ is appears in Hexagonal structure with a= b= 14.04, c= 8.601 respectively. The kinetics of the samples were studied using dynamic Seivert type apparatus. Kinetic curves of $NaAlH_4$ + x wt % $CeCl_3$ (x=1, 2) are shown in Fig (2) and Fig (3). Fig (2) is a curve for hydrogen desorption by $NaAlH_4$ + 1 wt % $CeCl_3$ and time at temperature 100^0 C – 250º C. $NaAlH_4$ + 1 wt % $CeCl_3$ sample desorbed 5.0 wt % hydrogen at temperature 250º C. 1 wt % $CeCl_3$ doped $NaAlH_4$ shows good desorption kinetic up to about 30 min at 250º C. After 30 min desorption rate is constant. Some wt % hydrogen released at 100º and 150º C. $CeCl_3$ is a good catalyst and good candidate for hydrogen desorption. In Fig. (3) Kinetic measurement for Desorption were determined using Dynamic seiverts and observed 2 wt % $CeCl_3$ doped $NaAlH_4$ released about 5.4 wt % hydrogen at 250º C. Kinetic curve of $NaAlH_4$ + 1:1 wt % $TiCl_3$+$CeCl_3$ at temperature range 100^0 C – 250º C is shown in Fig (4).The sample released 4.8 wt % hydrogen at temperature 250º C. Hydrogen capacity of sample is lower because $NaAlH_4$ partially decomposes. Amount of release hydrogen of $CeCl_3$ doped sodium alanate is low. Mixture of catalyst $TiCl_3$+$CeCl_3$ doped $NaAlH_4$ decreased amount of dehydrogen. The catalysts effective of $CeCl_3$ is more than $TiCl_3$.

IV. CONCLUSION

$NaAlH_4$+2 wt% $CeCl_3$ samples are milled in ball milling machine under argon atmosphere and analyzed by XRD with Powder X and PCPDWIN program.sodium alanate $NaAlH_4$ was found in Tetragonal structure with lattice constant a=b =5.02 and c=11.34 and Na_3AlH_6 is observed in cubic or monoclinic structure with lattice parameter a= b=c=7.755. Hydrogen is desorbed 4.8 wt % to 5.4 wt % at 250ºC with catalyst.Catalyst $CeCl_3$ is good for sodium alanate . Kinetics of catalyst is fast and very good for desorption. In brief, It has to conclude that enhanced storage capacity can be achieved and temperature is reduced 285ºC to 250 º C for desorption.

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REFERENCES

[1]. Orimo S, Nakamori Y, Eliseo JR, Zuttel A,Jensen CM. Complex hydrides forhydrogen storage . Chem Rev 2007 ; 107 : 411-32
[2]. Sakintuna B, Lamar Darkrim F, Hirscher M. Metal hydride materials for solid hydrogen storage : a review Int J hydrogen Energy 2007; 32 : 1121-40
[3]. Soloveichik GL, Gao Y Rijassenbeek J, Andrus M, kniajanski S, Bowman Jr RC,et al.Magnesium borohydride as a hydrogen storage material: properties and dehydrogen pathway of unsolved $Mg(BH_4)$. Int J Hydrogen Energy 2009 ; 34 :916 -28
[4]. Bogdanovic B, Schawickardi M. Ti doped alkali metal aluminium hydrides as potential novel reversible hydrogen storage materials. J. Alloys Compd 1997,253-254: 1-9
[5]. BogdanovicB, Brand RA, MarjanovicA, Schawickardi M. TolleJ .Metal dopedsodium aluminium hydrides as potential new hydrogen storage materials. Alloys Compd 2000, 302: 36-58.
[6]. B. Bogdanovic, M. Felderhoff,A.Pommerin, F. Schuth, N.Spielkamp. Advanced hydrogen storage materials based on Sc, Ce and Pr doped $NaAlH_4$. Adv. Mater 18 (2006)1198-1201
[7]. Durgun E, ciraci S Yildirim T. Function-metal atoms for hydrogen . Phys Rev B 2008; 77 (8) : 085405-13
[8]. Samanta A , Furuta T , Li J . Theoretical assessment of the elastic constants and hydrogen storage capacity of some metal organic frame work materials. J chem. Phys 2006 ; 125 (8) : 084714-21
[9]. W. Grochala , P.P. Edwards , Thermal Decomposition of the Non-Interstitial Hydrides for the Storage and Production of Hydrogen . Chem. Rev 104 (2004) 1283-1315
[10]. Zubizarreta L, Arenillas A , pis JJ. Carbon materials for H_2 storage. Int J hydrogen energy 2009; 34 (10) : 4575-81.
[11]. B. Bogdanovic , M. Felderhoff, A. pommerin , F. Schuth , N. Spielkamp, stark A. Cycling properties of Sc and Ce doped $NaAlH_4$ hydrogen storage materials prepared by the one step direct synthesis method. J. Alloys Comp 2009; 471: 383-6.
[12]. Xiulin Fan , Xuezhang Xiao, Lixin Chen, Shouquan Li, Qidong wang. Investigation on the nature of active species in the $CeCl_3$ doped sodium alante system. J. Alloys and Comp. 509S (2011) 5750-5753.
[13]. Borislav Bogdanovic , Michael felderhoff, Andre Pommerin. Cycling properties of Sc and Ce doped $NaAlH_4$ hydrogen storage materials prepared by the one step direct synthesis method J.alloy and comp. 471(2009) 383-386.

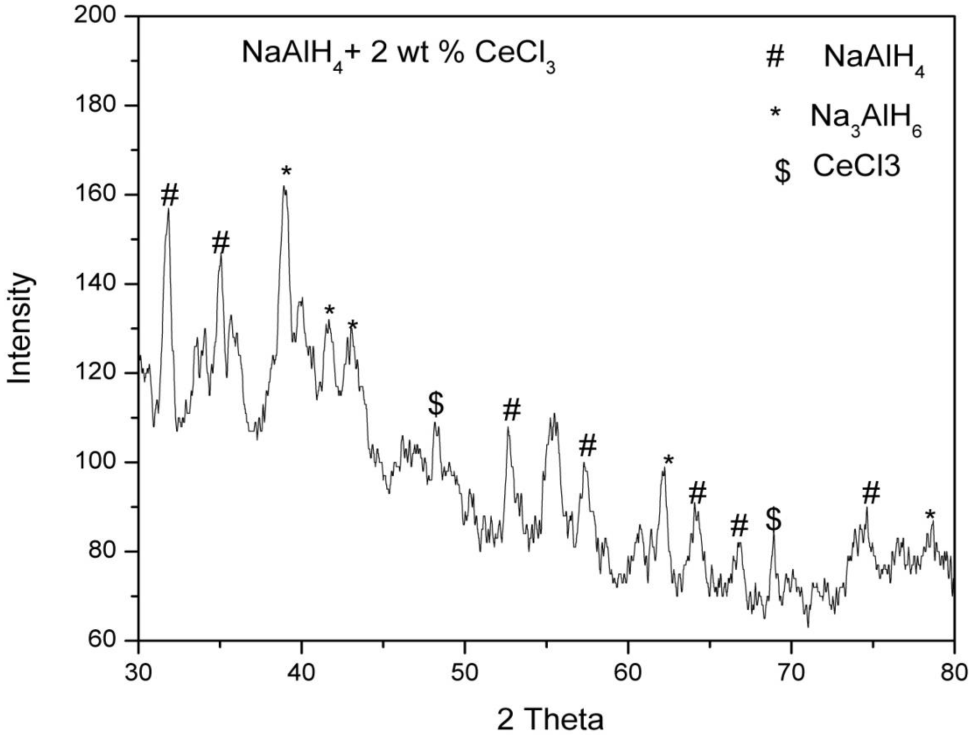

Fig 1:- XRD Patterns of 2mol% $CeCl_3$ doped $NaAlH_4$ at 250^0C

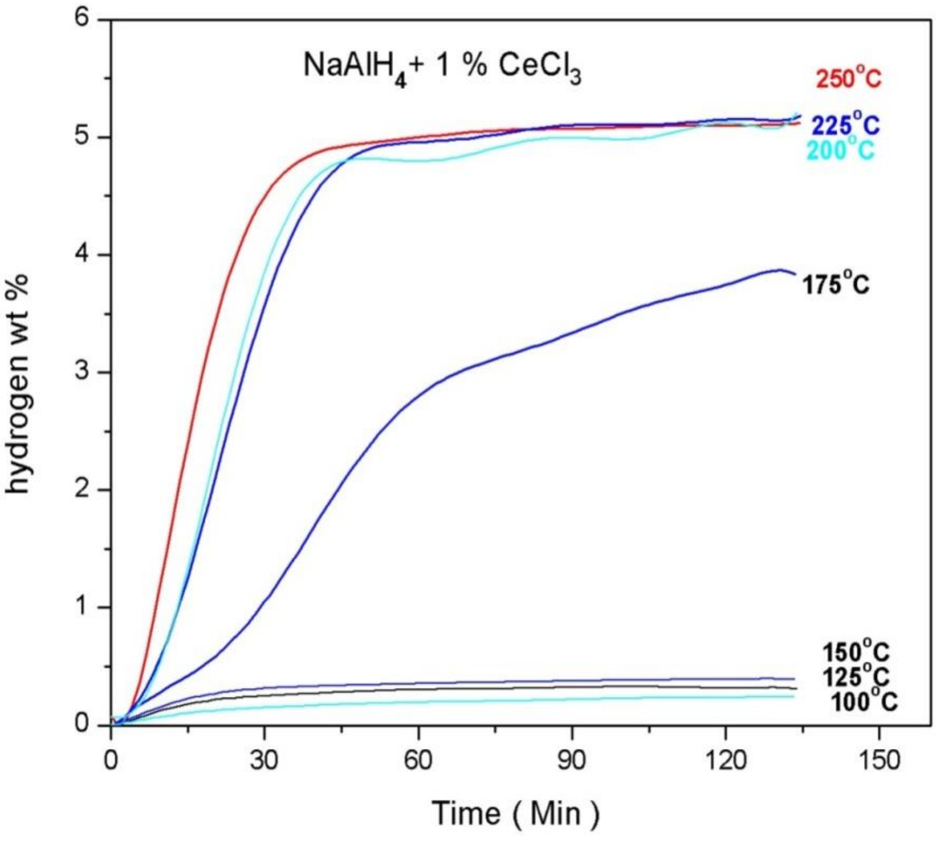

Fig 2:- Kinetic Curve of Sample $NaAlH_4$ with 1 wt % $CeCl_3$

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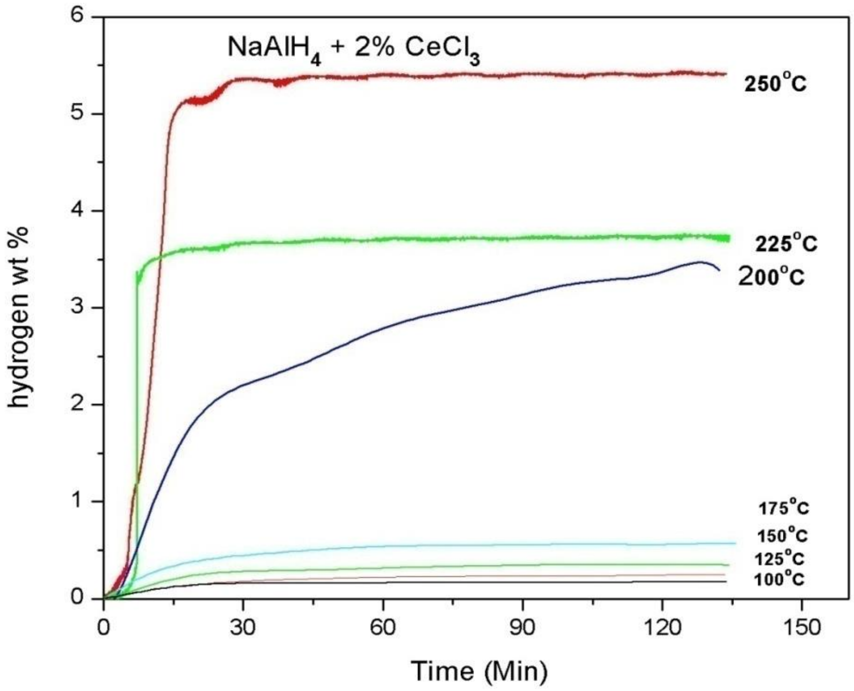

Fig 3:- Kinetic Curve of Sample $NaAlH_4$ with 2 wt % $CeCl_3$

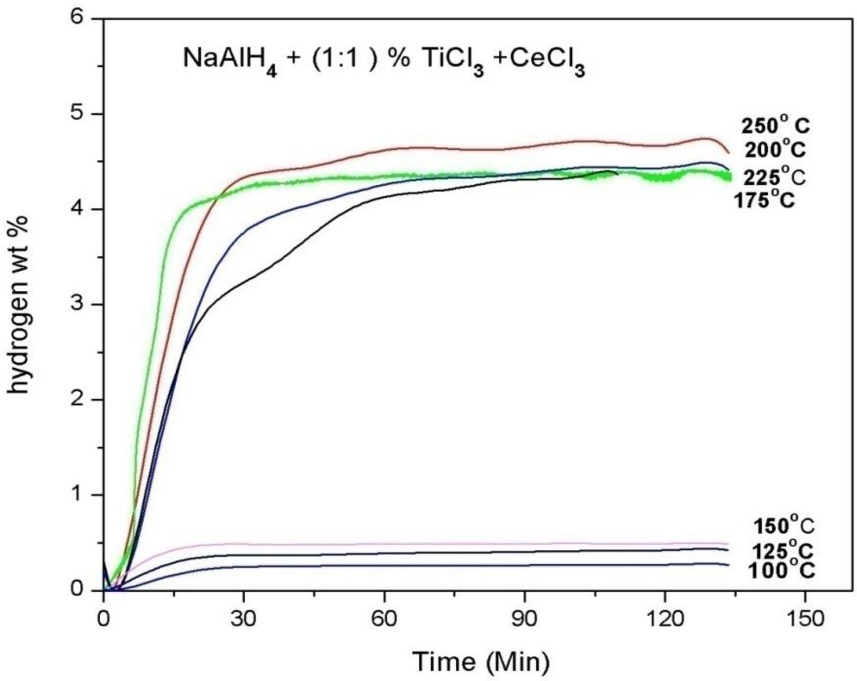

Fig 4:- Kinetic Curve of Sample $NaAlH_4$ with 1:1 $TiCl_3$+ $CeCl_3$